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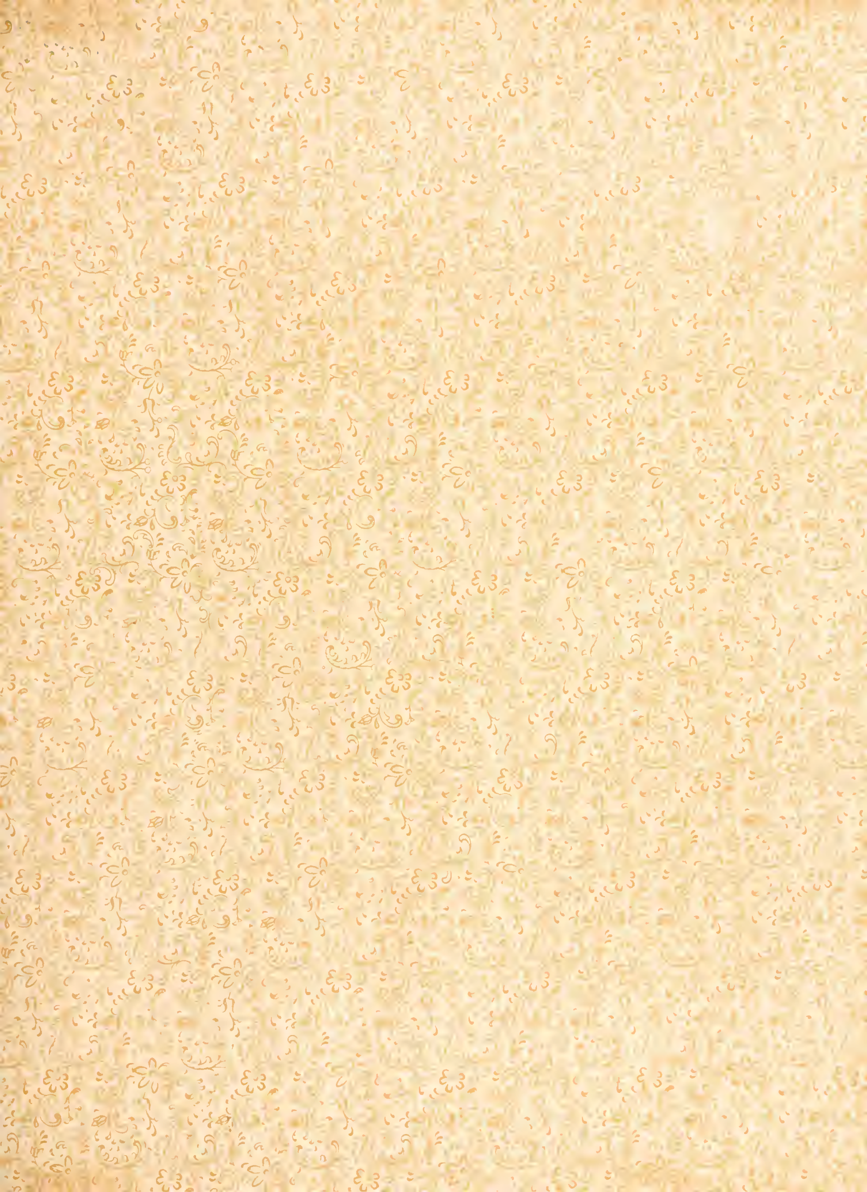

ESTERIFICATION LIMITS OF BENZOIC AND TOLUIC ACIDS WITH LOWER ALCOHOLS

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY

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This investigation was carried out under the advice and with the assistance of Professor Reid. I wish to take this opportunity to express to him my sincere appreciation of the help which he gave. I also feel under obligation to Professors Remsen, Morse, Jones, Gilpin, Frazer, and Lovelace for instruction and encouragement received from them.

HISTORICAL

Since the work of Berthelot and Péan de St. Gilles[1] in 1862, esterification has been one of the most frequently studied reactions. It has been regarded as one of the best examples of a reversible reaction, and has been commonly used to illustrate the mass law. However, calculation of the results obtained by these workers shows that they do not agree closely with the mass law. Their work was done almost exclusively with acids of the aliphatic series. They obtained 64.8 and 66.5 percent as the limits when methyl and ethyl alcohols were heated with benzoic acid in equivalent quantity, while with acetic acid the corresponding limits were 67.5 and 66.5 percent. Since ethyl alcohol gives sensibly the same limits with the two acids, their low result with methyl alcohol and benzoic acid seems doubtful. In fact in a study of the interdependence of limits[2] by Reid it was assumed that methyl and ethyl alcohols give the same limits with both acids. The first object of the present investigation was to obtain accurate values for the limits of benzoic and tolui acids with methyl ethyl and propyl alcohols. The second object was to ascertain how closely the esterification of benzoic acid by these alcohols obeys the mass law, when the proportions of acid and alcohol are varied and the third object was to study the effect of isomerism as illustrated by the three toluic acids.

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1. Ann.Chem. et Phys. (3) 65, 385(1862);66,5(1862);68,225 (1863).
2. Am. Chem. Jour. 45, 479 (1911).

MATERIALS.

ACIDS.

The benzoic, ortho and meta toluic acids were the commercial C.P. product, the para toluic acid was made by the Sandmeyer reaction. All were purified by boiling with animal charcoal, recrystallizing several times from boiling water (diluted alcohol for the toluic acids). They were then dried for one week in a vacuum dessicator.

ALCOHOLS.

The alcohols used were the C.P. commercial products. They were all refluxed with quick lime or metallic calcium until density determinations showed a water content of less than 0.04 percent.

ESTERS .

The esters were prepared by usual methods and carefully purified by washing drying and distillation.

STANDARD SOLUTIONS.

Standard HCl and $Ba(OH)_2$ were kept in large stock bottles directly connected to the burettes and protected from the air by a U-tube containing similar solutions. The barium hydroxide solution was in addition protected by soda lime.

The solutions were very nearly tenth normal, and the barium solution which was most subject to change, was restandardized about twice a month with the acids used in that period of time.

GLASS TUBES.

The tubing used was 6 mm in diameter, of Pyrex hard glass. Small tubes of 70 mm length were made. These were cleaned with chromic acid solution, boiled several hours in dilute HCl and then several hours each in two changes of distilled water. They were then thoroughly dried in an air oven at 150° and kept covered to protect from dust.

FURNACE.

The furnace used was an electrically heated and controlled tube furnace and having an average variation of ± 1°C. similar to that described by Pratt and Reid, but of better construction. It kept the desired temperature ± 1°.

PROCEDURE.

The tubes were weighed, partly filled with acid or ester drawn out and weighed again. The alcohol or water was then introduced to fill the tubes about two-thirds full. The tubes were then sealed off and the filled tube and tip weighed. Numbers

scratched on the tip and the tube, identified these during weighing and at titration. The tubes were then heated from two to eight days at 200° and after cooling, opened and titrated. The contents of the tube were nearly always liquid, which necessitated a different procedure from that used in former work done in this laboratory. The tubes were gently heated at the tip to drive from the tip any adherent liquid. They were then scored with a file and the tip broken off. The contents of the tube were then transferred to the flask by a capillary pipette and the tube and pipette washed out four times thoroughly with alcohol that had been distilled from KOH . The contents of the flask were then diluted to 25 cc. with the same alcohol. The acid remaining was then titrated using phenolphthalein indicator. An alcohol correction of 0.05 cc was deducted to correct for the acidity as determined for the amount of alcohol present.

EXPERIMENTAL.

In this investigation the points of interest were the limits of esterification and the effect of varying concentration of the reagents on the limits. The letters used in tabulating results are those usually found in text book expressions of the mass law.

A - Weight of alcohol or water in grams

B - Weight of acid or ester in gram

p - Active mass of alcohol or water in millimoles

q - Active mass of acid or ester in millimoles

alk - Cubic centimeters of standard alkali required in titration

x - Millimoles of reagents transformed when limit is reached, which is equivalent to the amount of ester and water formed in the acid series and the alcohol and acid formed in the ester series.

p-x Millimoles alcohol remaining (acid series) millimoles water remaining (ester series)

q-x Millimoles acid remaining (acid series) millimoles ester remaining (ester series)

$\sqrt{r}$ - The square root of the equilibrium constant

% - Percentage esterification calculated from formula given below

In the acid series at equilibrium we get from the titration the concentration of acid remaining, q-x, from which by subtraction we get, x, the concentration of the ester and water formed, and from this value that of the alcohol remaining, p-x. The equilibrium constant is then obtained.

$$\frac{\text{Water} \times \text{Ester}}{\text{Alcohol} \times \text{Acid}} = \frac{X^2}{(p-x)(q-x)} = r$$

In the ester series at equilibrium we get from the titration the concentration of acid and alcohol formed, x, which also by subtraction from the original concentrations of water and ester gives the concentrations of these untransformed,. From these data we obtain our equilibrium constant

$$\frac{\text{Alcohol x Acid}}{\text{Water x Ester}} = \frac{(p-x)(q-x)}{X^2} = r$$

To calculate the percentage of equivalent amounts esterified at limit we use the formula given by Reid:[1]

$$\% = \frac{100}{\sqrt{r}+1}$$

In the following tables the results are expressed in this percentage esterification at limit . The results in series I are the acid and ester sets of benzoic acid with methyl ethyl and propyl alcohols which have not been heated long enough to reach the limit, Series II expresses the same sets heated long enough to reach the limit. Series III, IV and V are the acid sets only of ortho meta and para toluic acids respectively, with the same alcohols, heated for eight days to insure reaching the limit of esterification.

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1. Am. Chem. Journal, 43, 499, (1910).

RESULTS.

SERIES I.- 48 HOURS AT 200° .

$CH_3OH + C_6H_5COOH$

A	0.16525	0.1697	0.18585	0.20815	0.1901
B	0.40965	0.3970	0.3635	0.3943	0.3345
p	5.1589	5.2978	5.8020	6.4982	5.9347
q	3.3565	3.2528	2.9783	3.2307	2.7407
alk.	6.19	5.47	4.31	4.45	3.51
x	2.7372	2.7062	2.5470	2.7858	2.3893
p-x	2.4217	2.5916	3.2550	3.7124	3.5454
q-x	0.6193	0.5466	0.4313	0.4449	0.3514
$\sqrt{r}$	2.2351	2.2737	2.1496	2.1677	2.1406
%	69.089	69.454	68.250	68.431	68.159

$H_2O + C_6H_5COOCH_3$

A	0.02815	0.0407	0.0944	0.12315	0.12525
B	0.6256	0.59535	0.5700	0.60815	0.56855
p	1.5625	2.2591	5.2398	6.8356	6.9522
q	4.5978	4.3755	4.1892	4.4696	4.1785
alk.	7.10	8.77	13.86	16.32	14.99
x	0.7098	0.8767	1.3856	1.6323	1.4993
p-x	0.8527	1.3824	3.8542	5.2033	5.4529
q-x	3.8880	3.4988	2.8036	2.8373	2.6792
$\sqrt{r}$	2.5652	2.5086	2.3779	2.3539	2.5493
%	71.951	71.499	70.395	69.977	71.825

$C_2H_5.OH + C_6H_5COOH$

A	0.3051	0.4716	0.3016	0.2965	0.3361
B	0.5211	0.6714	0.3735	0.3481	0.3485
p	6.6254	10.2410	6.5494	6.4387	7.2986
q	4.2696	5.5010	3.0602	2.8521	2.8554
alk.	9.30	10.05	4.76	4.34	3.85
x	3.3397	4.4961	2.5844	2.4181	2.4703
p-x	3.2857	5.7449	3.9650	4.0206	4.8283
q-x	0.9299	1.0049	0.4758	0.4340	0.3851
$\sqrt{r}$	1.9106	1.8713	1.8816	1.8306	1.8116
%	65.643	65.173	65.296	64.672	64.433

$H_2O + C_6H_5COO\ C_2H_5$

A	0.0779	0.1052	0.0732	0.1048	0.1038
B	0.7161	0.9449	0.6417	0.9168	0.7119
p	4.3239	5.8393	4.0631	5.8171	5.7615
q	4.7715	6.2960	4.2757	6.1087	4.7435
alk	15.31	20.48	14.57	19.39	17.73
x	1.5312	2.0475	1.4565	1.9389	1.7734
p-x	2.7927	3.7918	2.6066	3.8782	3.9881
q-x	3.2403	4.2485	2.8192	4.1698	2.9701
$\sqrt{r}$	1.9646	1.9686	1.8612	2.0740	1.9407
%	66.269	66.314	65.050	67.469	65.994

$C_3H_7OH + C_6H_5COO\ C_2H_5$

(96 HOURS AT 200°)

A	0.1304	0.2036	0.1782	0.2129	0.3041
B	0.5782	0.4674	0.3580	0.4014	0.3669
p	2.1710	3.3897	2.9635	3.5446	5.0629
q	4.7375	3.8296	2.9333	3.2889	3.0062
alk	28.70	14.31	9.61	10.13	5.83
x	1.8673	2.3991	1.9723	2.2756	2.4230
p-x	0.3037	0.9906	0.9912	1.2690	2.6399
q-x	2.8702	1.4305	0.9610	1.0133	0.5832
$\sqrt{r}$	2.0000	2.0154	2.0208	2.0068	1.9528
%	65.890	66.837	66.896	66.742	66.134

SERIES II.- 96 HOURS AT 200°.

$CH_3OH + C_6H_5COOH$

p	2.8846	3.6214	7.1585	4.9357	7.8265
q	4.7875	3.8444	3.7346	2.9230	4.1680
alk	23.61	12.43	5.48	4.59	5.48
x	2.4262	2.6019	3.6196	2.4645	3.6196
p-x	0.4584	1.0195	4.2069	2.4712	4.2069
q-x	2.3613	1.2425	0.5484	0.4585	0.5484
$\sqrt{r}$	2.3320	2.3118	2.3317	2.3153	2.3830
%	69.988	69.805	69.995	69.837	70.440

Mean, 70.013%

$H_2O + C_6H_5COO\ CH_3$

p	1.8706	2.1037	2.7309	4.9179	5.5284
q	4.0624	4.4023	4.0132	4.8955	4.4755
alk.	7.69	9.01	9.69	14.77	15.02
x	0.7694	0.9014	0.9693	1.4773	1.5020
p-x	1.1012	1.2023	1.7616	3.4406	4.0264
q-x	3.2930	3.5009	3.0439	3.4182	2.9735
$\sqrt{r}$	2.4750	2.2761	2.3890	2.3214	2.3037
%	70.553	69.476	70.493	69.892	69.731

Mean 70.029%

$C_2H_5OH + C_6H_5COOH$

p	2.6451	3.2379	4.2228	4.2955	4.1782
q	4.1943	3.2741	4.0963	3.3528	2.7342
alk.	20.89	11.12	13.36	8.85	6.01
x	2.1054	2.1618	2.7602	2.4679	2.1336
p-x	0.5397	1.0761	1.4626	1.8276	2.0446
q-x	2.0889	1.1123	1.3361	0.8849	0.6006
$\sqrt{r}$	1.9829	1.9760	1.9745	1.9406	1.9254
%	66.476	66.397	66.381	65.993	65.817

Mean 66.173%

$C_2H_5OH + C_6H_5COOH$

p	2.9860	3.7548	4.0230	4.0132	3.9676
q	5.1250	3.1209	3.2856	3.2495	3.0144
alk.	26.94	8.77	9.05	8.92	7.76
x	2.4309	2.2437	2.3811	2.3577	2.2389
p-x	0.5551	1.5111	1.6419	1.6555	1.7287
q-x	2.6941	0.8772	0.9045	0.8918	0.7755
$\sqrt{r}$	1.9878	1.9488	1.9539	1.9404	1.9337
%	66.531	66.088	66.146	65.991	65.913

Mean 66.173%

$H_2O + C_6H_5COO\ C_2H_5$

p	2.6726	5.1982	11.1012	10.7016	10.9958
q	3.2309	4.1808	6.4654	4.7688	4.6668
alk.	9.89	15.76	28.28	23.33	23.06
x	0.9885	1.5763	2.8277	2.3325	2.3056
p-x	1.6841	3.6219	8.2735	8.3691	8.6902
q-x	2.2424	2.6045	3.6382	2.4363	2.3612
$\sqrt{r}$	1.9659	1.9485	1.9403	1.9359	1.9647
%	66.283	66.084	65.990	65.938	66.270

Mean 66.174%

$H_2O + C_6H_5COO\ C_2H_5$

p	2.9557	2.8502	3.1139	3.3720	3.7078
q	3.0480	2.8981	2.9484	2.8608	3.1613
alk	10.10	9.70	10.25	10.49	11.54
x	1.0098	0.9699	1.0252	1.0489	1.1542
p-x	1.9459	1.8803	2.0887	2.3231	2.5536
q-x	2.0382	1.9282	1.9232	1.8119	2.0071
$\sqrt{r}$	1.9722	1.9632	1.9550	1.9560	1.9615
%	66.355	66.253	66.159	66.170	66.233

Mean 66.174%

$C_3H_7OH + C_6H_5COOH$

(144 HOURS AT 200°.)

p	3.4238	3.5154	2.9460	3.1600	4.5568
q	3.7248	3.3856	2.7796	2.7928	3.9157
alk	13.41	10.83	8.70	8.20	11.16
x	2.3838	2.3029	1.9093	1.9729	2.7997
p-x	1.0400	1.2125	1.0367	1.1871	1.7571
q-x	1.3410	1.0827	0.8703	0.8199	1.1160
$\sqrt{r}$	2.0185	2.0256	2.0101	2.0044	1.9993
%	66.871	66.949	66.779	66.715	66.582

Mean 66.779%

SERIES III.- 192 HOURS AT 200° .

$CH_3\ OH + OCH_3\ C_6H_4COOH$

p	6.8182	7.2084	7.9920
q	3.0280	2.8457	2.6712
alk	3.92	3.32	2.85
x	2.6365	2.5136	2.3859
p-x	4.1817	4.6948	5.6061
q-x	0.3915	0.3321	0.2853
$\sqrt{r}$	2.0606	2.0130	1.8865
%	67.327	66.810	65.356

mean 66.497%

$C_2H_5OH + O\ CH_3C_6H_4COOH$

p	3.5430	3.2618	3.8655	4.6430	5.1435
q	2.7733	2.4951	2.7877	2.0862	2.0149
alk	7.18	6.33	6.93	3.13	2.66
x	2.0551	1.8624	2.0944	1.7730	1.7485
p-x	1.4879	1.3994	1.7711	2.8700	3.3950
q-x	0.7182	0.6327	0.6933	0.3132	0.2664
$\sqrt{r}$	1.9880	1.9794	1.8901	1.8700	1.8386
%	66.533	66.436	65.399	65.157	64.771

Mean 65.659%

$C_3H_7OH + o\ CH_3C_6H_4COOH$

p	2.9194	3.6536	3.3248	3.5371	4.4636
q	2.9854	2.7752	2.2074	2.1622	2.7311
alk	10.08	6.78	4.64	4.17	5.30
x	1.9774	2.0975	1.7430	1.7455	2.2010
p-x	0.9420	1.5561	1.5818	1.7916	2.2626
q-x	1.0080	0.6777	0.4644	0.4167	0.5301
$\sqrt{r}$	2.0293	2.0425	2.0337	2.0202	2.0097
%	66.989	67.132	67.037	66.890	66.774

Mean, 66.964%

SERIES IV.- 192 HOURS AT 200°.

$CH_3OH + m\ CH_3C_6H_4COOH$

p	4.9700	3.9398	5.2494	4.6922	4.9107
q	3.4991	2.7105	3.2492	2.7009	2.4599
alk	7.57	5.80	6.19	4.50	3.59
x	2.7422	2.1309	2.6300	2.2509	2.1008
p-x	2.2278	1.8089	2.6194	2.4413	2.8099
q-x	0.7569	0.5796	0.6192	0.4500	0.3591
$\sqrt{r}$	2.1117	2.0811	2.0651	2.1475	2.0914
%	67.863	67.544	67.374	68.229 *	67.652

Mean, 67.608%

$C_2H_5OH + m\ CH_3C_6H_4COOH$

p	2.8492	3.1717	3.3443	3.2032	3.7428
q	2.6149	2.8461	2.6495	2.3140	2.4742
alk	8.19	8.73	7.25	5.72	5.65
x	1.7959	1.9731	1.9250	1.7425	1.9090
p-x	1.0533	1.1986	1.4193	1.4607	1.8338
q-x	0.8190	0.8730	0.7245	0.5715	0.5652
$\sqrt{r}$	1.9336	1.9289	1.8983	1.9071	1.8751
%	65.912	65.857	65.497	65.601	65.219

Mean, 65.617%

SERIES V.- 192 HOURS AT 200°.

$C_3H_7OH + m\ CH_3C_6H_4COOH$

p	2.4299	3.0284	3.4888	3.5446	3.6861
q	3.0838	2.9317	3.1007	2.6682	2.5878
alk	12.92	9.48	9.23	6.68	6.03
x	1.7923	1.9840	2.1773	2.0004	1.9848
p-x	0.6376	1.0444	1.3115	1.5442	1.7013
q-x	1.2915	0.9477	0.9234	0.6678	0.6030
$\sqrt{r}$	1.9751	1.9942	1.9785	1.9699	1.9596
%	66.388	66.602	66.426	66.329	66.212

Mean, 66.391 %

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* Not used in average.

$CH_3OH + p\ CH_3C_6H_4COOH$

p	3.7868	4.2379	4.9872	5.0044	5.3915
q	3.2036	2.5205	2.7932	2.1332	2.2317
alk	8.44	4.64	4.54	2.75	2.68
x	2.3594	2.0561	2.3396	1.8587	1.9635
p-x	1.4274	2.1818	2.6476	3.1457	3.4280
q-x	0.8442	0.4644	0.4536	0.2745	0.2682
$\sqrt{r}$	2.1493	2.0426	2.1349	2.0002	2.0431
%	68.247	67.132	68.101	66.669	67.139

Mean, 67.458%

$C_2H_5OH + p\ CH_3C_6H_4COOH$

p	3.9741	2.9860	3.4269	3.6440	4.6929
q	3.1360	2.0850	2.1949	2.2434	2.5363
alk	8.61	4.95	4.84	4.77	4.73
x	2.2747	1.5901	1.7107	1.7664	2.0629
p-x	1.6994	1.3959	1.7162	1.8776	2.6300
q-x	0.8613	0.4949	0.4842	0.4770	0.4734
$\sqrt{r}$	1.8823	1.9131	1.8766	1.8665	1.8488
%	65.305	65.672	65.237	65.114	64.897

Mean, 65.245%

$C_3H_7OH + p\ CH_3C_6H_4COOH$

p	2.5689	2.8886	2.9535	3.9208
q	2.5789	2.6848	2.2548	2.4275
alk	8.69	8.43	5.76	5.00
x	1.7095	1.8415	1.6788	1.9271
p-x	0.8594	1.0471	1.2747	1.8247
q-x	0.8694	0.8433	0.5760	0.5004
$\sqrt{r}$	1.9777	1.9597	1.9592	2.0170
%	66.417	66.213	66.207	66.855 *

Mean, 66.279%

SUMMARY OF RESULTS.

	Methyl	Ethyl	Propyl
Benzoic Acid	70.013	66.173	66.779
o.Toluic Acid	66.497	65.659	66.964
m.Toluic Acid	67.608	65.617	66.391
p.Toluic Acid	67.458	65.245	66.279

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* Not used in average.

DISCUSSION

The foregoing results furnish fairly concordant values for the limits of the various acids with corresponding alcohols. Since the experimental error is greater the further the ratio of alcohol to acid is from unity, to obtain the most reliable values for the limit, only those experiments have been considered in which the ratio of alcohol to acid was less than 1.5 . The limits are tabulated below .

	Methyl	Ethyl	Propyl
Benzoic Acid	69.98	66.22	66.78
o.Toluic Acid	67.07	66.12	66.72
m.Toluic Acid	67.70	65.62	66.39
p.Toluic Acid	68.17	65.36	66.28

For the purpose of showing the effect of varying ratio of alcohol to acid as influencing the equilibrium, the results have been arranged in the order of increasing proportion of alcohol.

Benzoic Acid.

Methyl Alcohol		Ethyl Alcohol		Propyl Alcohol	
Ratio	Limit	Ratio	Limit	Ratio	Limit
0.62	69.99	0.58	66.53	0.92	66.87
0.94	69.80	0.63	65.99	0.04	66.95
1.69	69.84	0.99	66.40	1.06	66.78
1.88	70.44	1.03	66.38	1.13	66.71
1.92	69.99	1.20	66.09	1.16	66.58
		1.22	66.15		
		1.23	65.99		
		1.28	65.99		
		1.32	65.91		
		1.53	65.82		

This effect was studied particularly with ethyl alcohol.

ETHYL ALCOHOL

o.Toluic Ratio	Acid Limit	m.Toluic Ratio	Acid Limit	p.Toluic Ratio	Acid Limit
1.28	66.53	1.09	65.91	1.27	65.30
1.31	66.44	1.11	65.86	1.43	65.67
1.39	65.40	1.26	65.50	1.56	65.24
2.23	65.16	1.38	65.60	1.62	65.11
2.55	64.77	1.52	65.22	1.85	64.90

From the tables above it appears that there is a drop in the limit with increase of the ratio of alcohol to acid. The drop is slight and not much beyond the unavoidable experimental error, but as the trend in all cases is in the same direction, it seems to be real.

The results of Berthelot and St. Gilles' work have been recalculated for comparison and are given below, the first two columns being their figures:-

	Ratio	%Esterification	$\sqrt{r}$	Limit
Methyl Alcohol and Benzoic Acid	1.0	64.8	1.841	64.80
	3.0	87.4	1.689	62.81
Ethyl Alcohol and Benzoic Acid	1.0	66.5	1.985	66.50
	2.0	83.1	1.870	66.15
	3.0	87.0	1.653	62.31
	4.0	89.3	1.549	60.77

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1. Ann de Chim et Phys (3) 68, 275-279 (1862)

	Ratio	% Esterification	$\sqrt{r}$	Limit
Methyl Alcohol and Acetic Acid	0.20	19.3	2.568	71.97
	0.45	39.0	2.287	69.58
	0.50	42.9	2.131	68.06
	0.67	54.6	2.301	69.71
	1.00	66.5	1.985	66.50
Ethyl Alcohol and Acetic Acid	1.00	67.5	2.077	67.50
	1.50	75.9	1.796	64.24
	2.00	84.0	1.951	66.10

It appears from the results that the change of the limit of esterification is in the same general direction, although some of the individual determinations are out of line.

From the above it appears that for esterification, the mass law holds very nearly but not quite accurately. The gas law holds for perfect gases only, and correction terms must be inserted on account of the mutual attraction of the particles and also because the particles are not infinitely small. The mass law in its simplest form tacitly assumes that the four substances A, B, C, and D have no influence whether on each other except that the reaction $A + B \rightleftarrows C + D$ takes place. This assumption though nearly correct in some cases, can never be absolutely so. Suppose for instance that C and A are very soluble in each other, more so than the other pairs; that is to say that A and C have an attraction for each other, which we may call physical, but it would have the effect of restraining the molecules of these two substances, so to speak, from taking part in the

reactions as they otherwise would and hence diminish their effective concentrations. While the mass law probably holds absolutely in ideal cases, in actual cases we expect only approximation such as we find with the gas law when actual gases are considered.

The effect of isomerism, in the acids, on the limit found with mercaptans and the three toluic acids was worked out by Sachs and Reid[1]. These authors found that the limit with ethyl mercaptan was practically the same with the ortho meta and para toluic acids. The results obtained above with alcohols, however, show a variation in the limit. With methyl alcohol the limit rises from ortho meta to para, while with ethyl and propyl alcohols the reverse is true. This exceptional behaviour of methyl is also observed in the high value of the limit with benzoic acid.

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[1] 1.- J. Am. Chem. Soc. 38, 2746 (1916).

CONCLUSION

1.- Esterification limits have been found for benzoic and the three toluic acids with methyl ethyl and propyl alcohols.

2.- The limits found vary only slightly with change of ratio of active masses, that is, the mass law holds very nearly.

3.- With the exception of methyl alcohol the esterification limit rises with increase of molecular weight of the alcohol.

4.- With methyl alcohol and toluic acids, para toluic acid shows the highest limit, ortho toluic the lowest.

5.- The reverse is true of ethyl and propyl alcohols and toluic acids.

6.- These acids have been found to react very slowly with alcohols even at 200° , four days being required to reach the limit.

BIOGRAPHY

Raymond Freas was born in York, Pennsylvania, January 23, 1886. He received his secondary education in the Baltimore City College and graduated from Wittenberg College, Springfield, Ohio in 1906 with the degree of A.B. He completed one year of graduate work at the University of Pennsylvania in 1908, and afterwards taught three years in Pennsylvania State College and the National Farm School, Farm School, Pennsylvania, and then entered the laboratory of the Baltimore Health Department as assistant chemist and later as assistant bacteriologist. He remained there until taking up graduate work in chemistry in the fall of 1915, where he has pursued his studies for the past two years. In his last year he was awarded a Hopkins Scholarship from Maryland .